

Sm-Fe-N SERIES COATED ALLOY POWDER FOR MAGNET AND PRODUCING METHOD THEREFOR

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Abstract of JP2001207201

PROBLEM TO BE SOLVED: To provide Sm-Fe-N series coated alloy powder for a magnet in which the heat resistance and corrosion resistance of Sm-Fe-N series alloy powder are improved, and simultaneously excellent in coercive force and saturation magnetization and to provide a method for producing the same. **SOLUTION:** Sm-Fe-N series alloy powder is mixed with the metal powder of Zn or the like having a melting point of 150 to 500 deg.C, this powdery mixture is subjected to heat treatment at 200 to 500 deg.C in inert gas, and at least a part of the surface of the alloy powder is coated with a metal such as Zn. After that, the obtained coated aggregate powder is subjected to wet or dry pulverizing, or a part of the metal coating the surface is dissolved in an acid or alkali solution to release the aggregation. The disaggregated Sm-Fe-N series coated alloy powder has saturation magnetization of 11 kG or more.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach at the Sm-Fe-N system alloy powder for magnets especially the Sm-Fe-N system covering alloy powder for magnets by which surface [a part of] was covered with metals, such as zinc, and a list.

[0002]

[Description of the Prior Art] As a high performance rare earth magnet, the Sm-Fe-N system magnet which has new chestnut ESHON type coercive force developmental mechanics is known. Furthermore, the rare earth magnet which has still higher magnetic properties as a magnet the various actuators for FA and for rotating machines is demanded by the end of today.

[0003] With such $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ (atomic ratio) alloy powder that is one of the Sm-Fe-N system magnets, maximum energy product (BH) max of 12MGOe extent and the coercive force of 8kOe extent are acquired by considering as a resin BONDETTO magnet with several microns single crystal powder. However, the thermal resistance and corrosion resistance of Sm-Fe-N system alloy powder are inferior as compared with the Sm-Co system alloy powder and Nd-Fe-B system alloy powder which are other rare earth magnet powder.

[0004] Then, in order to raise the thermal resistance and corrosion resistance of Sm-Fe-N system alloy powder, various researches are done briskly. Coercive force of the alloy powder by which it was indicated by it that high coercive force is acquired, for example, Zn coating was carried out to it with the heat CVD method also in it at the same time it had improved thermal resistance and corrosion resistance to JP,4-338603,A by performing metal coatings, such as Zn, to $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ alloy powder is set to 12kOe(s).

[0005]

[Problem(s) to be Solved by the Invention] Although coercive force with the Sm-Fe-N system alloy powder expensive [that thermal resistance and corrosion resistance are improved] which performed metal coatings, such as Zn, is acquired as described above, saturation magnetization is about 10 or less kGs, and will fall more sharply than the Sm-Fe-N system alloy powder before coating. Since the projection to which this lowers coercive force by metal coating is graduated, coercive force becomes high, but since it was mutually joined with the metal by which coating was carried out and powder condensed, it is thought that saturation magnetization fell without making powdered

orientation.

[0006] For this reason, although research for obtaining the magnet powder which controlled the fall of saturation magnetization as much as possible, and was excellent in magnetic properties is briskly done, without causing powdered condensation while acquiring high coercive force in case Sm-Fe-N system alloy powder is coated with metals, such as Zn, the still practical approach is not established.

[0007] This invention aims at offering the Sm-Fe-N system covering alloy powder for magnets excellent in coercive force and saturation magnetization, and its manufacture approach at the same time it improves the thermal resistance and corrosion resistance of Sm-Fe-N system alloy powder in view of such a conventional situation.

[0008]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention is covered with the metal a part of whose front face [at least] of Sm-Fe-N system alloy powder is the melting point of 150-500 degrees C, and offers the Sm-Fe-N system covering alloy powder for magnets characterized by saturation magnetization being 11 or more kGs.

[0009] Moreover, after the manufacture approach of the above-mentioned Sm-Fe-N system covering alloy powder for magnets mixes Sm-Fe-N system alloy powder and metal powder with a melting point of 150-500 degrees C, heat-treats them at 200-500 degrees C among inert gas and covers a part of front face [at least] of alloy powder with a metal, it is characterized by solving the obtained condensation in the end of covering agglomerated powder.

[0010] In the manufacture approach of this Sm-Fe-N system covering alloy powder for magnets, there is an approach of grinding the end of covering agglomerated powder in wet or dry type or the approach of dissolving some metals which have covered the front face in the end of covering agglomerated powder in an acid or the solution of alkali as an approach of solving the condensation in the end of covering agglomerated powder.

[0011]

[Embodiment of the Invention] In this invention, the front face of alloy powder can be easily covered with the metal of the low-melt point describing above by heat-treating Sm-Fe-N system alloy powder and metal powder with a melting point of 150-500 degrees C in inert gas. Since it will be in the condition that powder joined mutually and they condensed the end of covering agglomerated powder it was covered with the metal of the low-melt point describing above, it will not become one particle at a time with a lump at the time of powder orientation, therefore magnetic properties will fall. Then, outstanding magnetic properties are acquired by dispelling the state of aggregation in the end of covering agglomerated powder mutually condensed by covering of the above-mentioned metal even in the condition that each particle can blend substantially.

[0012] That is, in surface discontinuity's, such as a projection, being graduated by shaping of metallic coating, the particle of Sm-Fe-N system alloy powder is considered that high coercive force is acquired in order to decrease, when the nucleus of reverse magnetic-domain generating carries out a diffusion reaction with a covering metal. On the other hand, although magnetic properties fall since each particle condenses by metallic coating, by solving powdered condensation by approaches, such as grinding, high magnetic properties are acquired and especially the fall of saturation magnetization can be controlled effectively.

[0013] Covering on the front face of a particle being possible, and being able to restore surface discontinuity, such as a projection, flat and smooth by heat treatment, as a metal which covers Sm-Fe-N system alloy powder, and a diffusion layer's being formed between a covering metal and alloy powder, and the ingredient which is easy to solve condensation according to a covering metal further are desirable. As such a covering metal, a low-melt point metal [that the melting point is 150-500 degrees C] metal (Zn), for example, zinc, tin (Sn), an indium (In), lead (Pb), etc. are mentioned. Since especially Zn tends to make Fe and Sm, and an alloy from the temperature of 420 degrees C or more, it is desirable.

[0014] The content of a covering metal with a melting point [in Sm-Fe-N system covering alloy powder] of 150-500 degrees C has 0.1 - 9.1% of the weight of the desirable range. It runs short of that the content of this covering alloy covers Sm-Fe-N system alloy powder with less than 0.1 % of the weight, iH_c (coercive force) does not go up, but saturation magnetization will be set to less than 11 kGs if 9.1 % of the weight is exceeded conversely. Moreover, generally the range of the thickness of a metal with a melting point of 150-500 degrees C which has covered the front face of Sm-Fe-N system alloy powder is 10-5000Å on an average. For example, when 5% of the weight of Zn powder is added to Sm-Fe-N system alloy powder with a particle size of 5 micrometers, the thickness of Zn covering becomes about 440Å.

[0015] The approach of covering Sm-Fe-N system alloy powder with a metal mixes the coarse powder end of a Sm-Fe-N system alloy, or impalpable powder with the metal powder of low-melt point points, such as Above Zn, and heat-treats it at 200-500 degrees C in inert gas, such as N₂ gas and Ar gas. If the reaction of metal powder and Sm-Fe-N system alloy powder does not progress at less than 200 degrees C but heat treatment temperature exceeds 500 degrees C conversely, Sm-Fe-N system alloy powder will decompose. In addition, as for the addition of the metal powder to Sm-Fe-N system alloy powder, it is desirable to add 0.1 - 10% of the weight of metal powder to Sm-Fe-N system alloy powder generally so that the content of a covering metal may become 0.1 - 9.1% of the weight of covering alloy powder, as mentioned above.

[0016] Although a metal is covered with this heat treatment by a part of front face [at least] of Sm-Fe-N system alloy powder, since alloy powder is condensing with this covering metal, it is necessary to solve that end of covering agglomerated powder it condensed. What is necessary is for there to be especially no limit in the approach of solving the condensation in the end of covering agglomerated powder, and just to choose it as it suitably according to extent of condensation, or the quality of the material of a covering metal.

[0017] There is the approach of cracking the end of covering agglomerated powder it condensed in wet or dry type as one of the desirable approaches for solving condensation. For example, condensation of covering alloy powder can be solved by grinding 150 to 300 rpm in a solvent by attritor for 5 minutes to 3 hours. Moreover, the condensation in the end of covering agglomerated powder can be solved by beginning to melt a covering metal, using the solution of an acid or alkali as the condensation in the end of covering agglomerated powder, and an option to solve.

[0018] In addition, you may be the alloy presentation which consists of the alloy presentation currently generally used as an object for magnets, at least one sort of rare earth elements 5 which specifically use Sm as an essential element - 15 atom %, nitrogen

0.5 - 25 atom %, and iron that permuted iron or some of remainder with cobalt about Sm-Fe-N system alloy powder although there is especially no limit. Moreover, especially the manufacturing method of this Sm-Fe-N system alloy powder cannot be limited, either, for example, Sm-Fe alloy powder can be manufactured by reduction diffusion method which is indicated by a dissolution alloying method or JP,3-62764,B, and this Sm-Fe alloy powder can be nitrided and manufactured after that. Furthermore, after nitriding the sintered compact obtained, application, i.e., the reduction diffusion reaction, of a reduction diffusion method which is indicated by JP,5-148517,A, a wet process can be carried out and it can also manufacture. Especially in these approaches, application of a reduction diffusion method is excellent in respect of the manufacturing cost.

[0019] Thus, since the Sm-Fe-N system covering alloy powder of this invention obtained has been independent in the condition that high coercive force is acquired, powdered condensation is moreover solved, and the orientation of each particle can be carried out substantially at the same time it is equipped with the thermal resistance and corrosion resistance which were excellent with formation of metallic coating, such as Zn, it has the high saturation magnetization exceeding 11kG.

[0020]

[Example] The Sm-Fe alloy powder which contains 25% of the weight of Sm by the example 1 reduction diffusion method was manufactured. That is, the granular metal calcium of 99 % of the weight of purity was mixed with the electrolysis Fe powder below 99.9 % of the weight of purity, and 150 meshes (it is the same a standard [for Tyler] one, and the following) of grain size, and the oxidization Sm powder of 99 % of the weight of purity, and 325 meshes of average grain size using V blender. The obtained mixture is put into a stainless steel container, in Ar ambient atmosphere, at 1150 degrees C, it heated for 8 hours and the reduction diffusion reaction was carried out.

Subsequently, this resultant is cooled, it supplied underwater and it was collapsed. After removing CaO which rinsed the obtained slurry and carried out acid cleaning using the acetic acid further and which carried out the byproduction to unreacted calcium, it filtered, the vacuum drying was permuted and carried out by ethanol, and 25-% of the weight Sm-Fe alloy powder with a particle size of 150 micrometers or less was obtained.

[0021] It cooled and took out, after nitriding by holding this Sm-Fe alloy powder at 480 degrees C in a sieve part opium poppy and hydrogen-ammonia mixed gas to 100 micrometers or less for 270 minutes. For Sm, Fe was [N of the presentation of the obtained Sm-Fe-N alloy powder] 3.5 % of the weight 72.4% of the weight 24.1% of the weight.

[0022] Zn powder of the addition shown in the following table 1 to 1kg of this Sm-Fe-N alloy powder was mixed, and it ground [further] to serve both as 200rpm and 60-minute mixing by attritor. Then, Ar gas was taken out, after heat-treating at 430 degrees C with the sink for 10 hours and cooling to a room temperature by 1l. / min. Further, since the front face was covered with Zn and it was condensing the end of covering agglomerated powder it was obtained, after grinding for 20 minutes, it dried and Sm-Fe-N system covering alloy powder was obtained 200 rpm, in the solvent, by attritor. About the Sm-Fe-N system covering alloy powder after the covering agglomerated powder end immediately after heat treatment, and grinding, magnetic properties were measured by VSM, respectively and the result was shown in the following table 1.

[0023]

[Table 1]

Zn addition Covering agglomerated powder end immediately after heat treatment
 Covering agglomerated powder end after grinding Sample (wt%) Saturation
 magnetization (kG) Coercive force (kOe) Saturation magnetization (kG) Coercive force
 (kOe) 1* 0 14.3 7.2 12.9 8.8 2* 0.05 14.3 7.2 13.0 8.7 3 1 10.6 9.3 12.8 10.5 4 2 10.2 9.6
 12.5 11.0 5 39.2 10.4 11.8 11.7 6 4 8.9 11.0 11.5 12.4 7 8.4 12.4 11.3 14.5 8 10 7.9
 15.1 11.1 17.8 9* 12 7.5 17.1 10.7 18.9 (notes) The sample which attached * of front
 Naka is an example of a comparison.

[0024] Although the samples 3-8 of this invention are high [coercive force] about 2-8
 kOes in the end of the covering agglomerated powder immediately after heat treatment as
 compared with the sample 1 which does not add Zn, and the sample 2 with few Zn
 additions, saturation magnetization is low a maximum of 6.4 kG for condensation, so that
 the result of the above-mentioned table 1 may show. However, with the covering alloy
 powder of samples 3-8 with which the condensation after grinding was solved, 11.1-
 12.8kG and high saturation magnetization were obtained. Moreover, the saturation
 magnetization of the sample 9 with many additions of Zn is less than 11 kGs.

[0025] The end of covering agglomerated powder Zn was covered to Sm-Fe-N system
 alloy powder like the example 2 above-mentioned example 1 was produced, and after
 supplying in 200ml of acetic-acid water solutions which thinned 10g with pure water 100
 times in this end of covering agglomerated powder and agitating for 3 minutes, the Sm-
 Fe-N system covering alloy powder with which it dried and condensation was solved was
 obtained. Although the saturation magnetization in the above-mentioned end of covering
 agglomerated powder was 10.2kG(s), the saturation magnetization of the covering alloy
 powder with which condensation was solved was raised to 12.8kG(s).

[0026] In order to check the thermal resistance of the Sm-Fe-N system covering alloy
 powder of each sample finally obtained in the example 3 above-mentioned example 1,
 10g of each sample was paid to oven, and it held at 230 degrees C in the vacuum for 1
 hour. Then, magnetic properties were measured like [powder / after a heat resistance test
 / covering alloy] the example 1, and the result was shown in the following table 2.

[0027]

[Table 2]

Zn addition Covering agglomerated powder end after grinding Covering alloy powder
 after a heat test Sample (wt%) Saturation magnetization (kG) Coercive force (kOe)
 Saturation magnetization (kG) Coercive force (kOe) 1* 0 12.9 8.8 12.4 6.1 2* 0.05 13.0
 8.7 12.4 6.2 3 1 12.8 10.5 12.5 9.2 4 2 12.5 11.0 12.2 9.8 5 3 11.8 11.7 11.5 10.3 6 4 11.5
 12.4 11.3 11.0 7 11.3 14.5 11.2 13.4 8 10 11.1 17.8 11.1 16.7 9* 12 10.7 18.9 10 7 18.7
 (notes) The sample which attached * of front Naka is an example of a comparison.

[0028] The result of the above-mentioned table 2 shows that thermal resistance of the
 samples 3-8 of this invention is improving by Zn covering. That is, by the samples 3-8 of
 this invention which performed Zn covering to the coercive force after a heat test
 declining to 6.1-6.2kOe by the sample 1 which has not given Zn covering, and the sample
 2 with few Zn additions, the coercive force of 9 or more kOes is maintained.

[0029] in order [furthermore,] to check the corrosion resistance of the Sm-Fe-N system
 covering alloy powder of each sample finally obtained in the above-mentioned example 1
 -- 10g of each sample -- the constant temperature of 70 degrees C and 80% of humidity --
 it put into the constant humidity chamber and held for 10 hours. Then, magnetic

properties were measured like [powder / after a corrosion resistance test / covering alloy] the example 1, and the result was shown in the following table 3.

[0030]

[Table 3]

Zn addition Covering agglomerated powder end after grinding Covering alloy powder after a corrosion test Sample (wt%) Saturation magnetization (kG) Coercive force (kOe) Saturation magnetization (kG) Coercive force (kOe) 1* 0 12.9 8.8 12.1 5.8 2* 0.05 13.0 8.7 12.1 5.9 3 1 12.8 10.5 12.2 8.2 4 2 12.5 11.0 12.0 9.0 5 3 11.8 11.7 11.4 9.5 6 4 11.5 12.4 11.1 10.2 7 7 11.3 14.5 11.1 12.1 8 10 11.1 17.8 11.0 14.9 9* 12 10.7 18.9 10.5 16.9 (notes)

The sample which attached * of front Naka is an example of a comparison.

[0031] The corrosion resistance improvement of the samples 3-8 of this invention is more distinct than the result of the above-mentioned table 3 by Zn covering. That is, by the samples 3-8 of this invention which performed Zn covering to the coercive force after ***** declining to 5.8-5.9kOe by the sample 1 which has not covered Zn, and the sample 2 with few Zn additions, the coercive force of 8 or more kOes is maintained also even for after the corrosion resistance test.

[0032] Although Sm-Fe-N system covering alloy powder was manufactured like the example 4 aforementioned example 1, the metal powder which carries out addition mixing used Zn powder, In powder, or Sn powder, and made the addition 3 % of the weight. About each obtained covering alloy powder, magnetic properties were measured like the example 1 and the result was shown in the following table 4.

[0033]

[Table 4]

Covering agglomerated powder end immediately after heat treatment Covering agglomerated powder end after grinding Sample Addition metal Saturation magnetization (kG) Coercive force (kOe) Saturation magnetization (kG) Coercive force (kOe) 10* Nothing 14.3 7.2 12.9 8.8 11 Zn 9.2 10.4 11.8 11.7 12 In 9.8 8.2 12.3 9.9 13 Sn 9.3 7.8 12.0 9.5 (notes) The sample which attached * of front Naka is an example of a comparison.

[0034] Although the samples 11-13 of this invention are high [coercive force] about 1-3 kOes in the end of the covering agglomerated powder immediately after heat treatment as compared with the sample 10 which does not add the metal powder of a low-melt point point, saturation magnetization is low a maximum of 5 kG for condensation, so that the result of the above-mentioned table 4 may show. However, with the covering alloy powder of samples 11-13 with which the condensation after grinding was solved, the high saturation magnetization of 11.8-12.3kG was obtained.

[0035] In order to check the thermal resistance of the Sm-Fe-N system covering alloy powder of each sample obtained above, like said example 3, 10g of each sample was paid to oven, and it held at 230 degrees C in the vacuum for 1 hour. Then, about the covering alloy powder after a heat resistance test, magnetic properties were measured like the above-mentioned example 1, and the result was shown in the following table 5.

[0036]

[Table 5]

Covering agglomerated powder end after grinding Covering alloy powder sample after a heat test Addition metal Saturation magnetization (kG) Coercive force (kOe) Saturation magnetization (kG) Coercive force (kOe) 10* Nothing 12.9 8.8 12.4 6.1 11 Zn 11.8 11.7

11.5 10.3 12 In 12.3 9.9 12.1 8.8 13 Sn 12.0 9.5 11.9 8.5 (notes) The sample which attached * of front Naka is an example of a comparison.
 [0037] As for each sample of this invention, it is more distinct than the result of the above-mentioned table 5 that thermal resistance improved by covering of Zn, In, and Sn. That is, as compared with the sample 10 which has not covered, about 2.4-4 kOes of coercive force after a heat test are high by the samples 11-13 of this invention which covered Zn, In, and Sn.

[0038] in order [furthermore,] to check the corrosion resistance of the Sm-Fe-N system covering alloy powder of each sample obtained above -- said example 3 -- the same -- 10g of each sample -- the constant temperature of 70 degrees C and 80% of humidity -- it put into the constant humidity chamber and held for 10 hours. Then, magnetic properties were measured like [powder / after a corrosion resistance test / covering alloy] the example 1, and the result was shown in the following table 6.

[0039]

[Table 6]

Covering agglomerated powder end after grinding Covering alloy powder sample after a corrosion test Addition metal Saturation magnetization (kG) Coercive force (kOe)
 Saturation magnetization (kG) Coercive force (kOe) 10* Nothing 12.9 8.8 12.1 5.8 11 Zn
 11.8 11.7 11.4 9.5 12 In 12.3 9.9 12.1 9.1 13 Sn 12.0 9.5 11.9 8.8 (notes) The sample which attached * of front Naka is an example of a comparison.

[0040] The corrosion resistance improvement of each sample of this invention is more distinct than the result of the above-mentioned table 6 by covering of Zn, In, and Sn. That is, as compared with the sample 10 which has not covered, about 3-3.5 kOes of coercive force after a corrosion test are high by the samples 11-13 of this invention which covered Zn, In, and Sn.

[0041]

[Effect of the Invention] While excelling in thermal resistance and corrosion resistance by being able to form metallic coating, such as Zn, in the front face of the Sm-Fe-N system alloy powder which has new chestnut ESHON type coercive force developmental mechanics easily, and solving the condensation in the end of covering agglomerated powder by which metallic coating was carried out further by grinding etc. according to this invention, the Sm-Fe-N system covering alloy powder which has the high saturation magnetization which the high coercive force of 8 or more kOes is acquired, and exceeds 11kG(s) can be offered cheaply. Therefore, this covering alloy powder is magnet powder of the Sm-Fe-N system excellent in the magnetic properties which have new chestnut ESHON type coercive force developmental mechanics, and is promising as an object for magnets the various actuators for FA, and for rotating machines.

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CLAIMS

[Claim(s)]

[Claim 1] Sm-Fe-N system covering alloy powder for magnets which is covered with the metal a part of whose front face [at least] of Sm-Fe-N system alloy powder is the melting point of 150-500 degrees C, and is characterized by saturation magnetization being 11 or more kGs.

[Claim 2] Sm-Fe-N system covering alloy powder for magnets according to claim 1 characterized by the presentation of said Sm-Fe-N system alloy powder consisting of at least one sort of rare earth elements 5 which use Sm as an essential element - 15 atom %, nitrogen 0.5 - 25 atom %, and iron that permuted iron or some of remainder with cobalt.

[Claim 3] Sm-Fe-N system covering alloy powder for magnets according to claim 1 or 2 characterized by the content of a metal with a melting point [said] of 150-500 degrees C being 0.1 - 9.1 % of the weight.

[Claim 4] Sm-Fe-N system covering alloy powder for magnets according to claim 1 to 3 with which thickness of a metal with a melting point [said] of 150-500 degrees C which covers the front face of said Sm-Fe-N system alloy powder is characterized by being 10-5000A on an average.

[Claim 5] Sm-Fe-N system covering alloy powder for magnets according to claim 1 to 3 characterized by manufacturing said Sm-Fe-N system alloy powder by the reduction diffusion method.

[Claim 6] The manufacture approach of the Sm-Fe-N system covering alloy powder for magnets characterized by solving the obtained condensation in the end of covering agglomerated powder after mixing Sm-Fe-N system alloy powder and metal powder with a melting point of 150-500 degrees C, heat-treating at 200-500 degrees C among inert gas and covering a part of front face [at least] of alloy powder with a metal with a melting point [said] of 150-500 degrees C.

[Claim 7] adding said metal powder 0.1 to 10% of the weight to said Sm-Fe-N system alloy powder -- the manufacture approach of the Sm-Fe-N system covering alloy powder for magnets according to claim 6 characterized by things.

[Claim 8] The manufacture approach of the Sm-Fe-N system covering alloy powder for magnets according to claim 6 or 7 characterized by solving the condensation in the end of covering agglomerated powder by grinding said end of covering agglomerated powder in wet or dry type.

[Claim 9] The manufacture approach of the Sm-Fe-N system covering alloy powder for magnets according to claim 6 or 7 characterized by solving the condensation in the end of covering agglomerated powder by dissolving some metals which have covered said front face in the end of covering agglomerated powder in an acid or the solution of alkali.

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最終頁に続く

(54) 【発明の名称】 磁石用 Sm-Fe-N 系被覆合金粉末及びその製造方法

(57) 【要約】

【課題】 Sm-Fe-N 系合金粉末の耐熱性及び耐食性を改善すると同時に、保磁力及び飽和磁化にも優れた磁石用 Sm-Fe-N 系被覆合金粉末、及びその製造方法を提供する。

【解決手段】 Sm-Fe-N 系合金粉末に融点 150～500℃ の Zn 等の金属粉末を混合し、不活性ガス中 200～500℃ で熱処理して合金粉末の表面の少なくとも一部を Zn 等の金属で被覆する。その後、得られた被覆凝集粉末を湿式又は乾式にて粉碎するか、又は表面を被覆している金属の一部を酸又はアルカリ溶液中で溶解して凝集を解く。凝集が解かれた Sm-Fe-N 系被覆合金粉末は、飽和磁化が 1.1 kG 以上である。

【特許請求の範囲】

【請求項1】 Sm-Fe-N系合金粉末の表面の少なくとも一部が融点150～500℃の金属で被覆され、飽和磁化が11kG以上であることを特徴とする磁石用Sm-Fe-N系被覆合金粉末。

【請求項2】 前記Sm-Fe-N系合金粉末の組成が、Smを必須元素とする少なくとも1種の希土類元素5～15原子%と、窒素0.5～2.5原子%と、残部の鉄又は一部をコバルトで置換した鉄とからなることを特徴とする、請求項1に記載の磁石用Sm-Fe-N系被覆合金粉末。

【請求項3】 前記融点150～500℃の金属の含有量が0.1～9.1重量%であることを特徴とする、請求項1又は2に記載の磁石用Sm-Fe-N系被覆合金粉末。

【請求項4】 前記Sm-Fe-N系合金粉末の表面を被覆する前記融点150～500℃の金属の厚みが、平均で10～5000Åであることを特徴とする、請求項1～3のいずれかに記載の磁石用Sm-Fe-N系被覆合金粉末。

【請求項5】 前記Sm-Fe-N系合金粉末が還元拡散法で製造されたものであることを特徴とする、請求項1～3のいずれかに記載の磁石用Sm-Fe-N系被覆合金粉末。

【請求項6】 Sm-Fe-N系合金粉末と融点150～500℃の金属粉末を混合し、不活性ガス中200～500℃で熱処理して合金粉末の表面の少なくとも一部を前記融点150～500℃の金属で被覆した後、得られた被覆凝集粉末の凝集を解くことを特徴とする磁石用Sm-Fe-N系被覆合金粉末の製造方法。

【請求項7】 前記Sm-Fe-N系合金粉末に対して前記金属粉末を0.1～10重量%添加することことを特徴とする、請求項6に記載の磁石用Sm-Fe-N系被覆合金粉末の製造方法。

【請求項8】 前記被覆凝集粉末を湿式又は乾式にて粉砕することにより、被覆凝集粉末の凝集を解くことを特徴とする、請求項6又は7に記載の磁石用Sm-Fe-N系被覆合金粉末の製造方法。

【請求項9】 前記被覆凝集粉末の表面を被覆している金属の一部を酸又はアルカリの溶液中で溶解することにより、被覆凝集粉末の凝集を解くことを特徴とする、請求項6又は7に記載の磁石用Sm-Fe-N系被覆合金粉末の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、磁石用のSm-Fe-N系合金粉末、特に表面の一部が亜鉛などの金属で被覆された磁石用Sm-Fe-N系被覆合金粉末、並びにその製造方法に関する。

【0002】

【従来の技術】 高性能希土類磁石として、ニュークリエーションタイプの保磁力発生機構を有するSm-Fe-N系磁石が知られている。更に今日では、各種FA用アクチュエーターや回転機用の磁石として、より一層高い磁気特性を有する希土類磁石が要望されている。

【0003】 このようなSm-Fe-N系磁石の一つであるSm₂Fe₁₇N₃（原子比）合金粉末では、数ミクロンの単結晶粉末で樹脂ボンデッド磁石とすることにより、12MGOe程度の最大エネルギー積(BH)_{max}と、8kOe程度の保磁力が得られている。しかしながら、Sm-Fe-N系合金粉末の耐熱性及び耐食性は、他の希土類磁石粉末であるSm-Co系合金粉末やNd-Fe-B系合金粉末に比較して劣っている。

【0004】 そこで、Sm-Fe-N系合金粉末の耐熱性及び耐食性を向上させるため、種々の研究が盛んに行われている。その中でも、特開平4-338603号公報には、Sm₂Fe₁₇N₃合金粉末にZnなどの金属コーティングを行うことにより、耐熱性と耐食性を改善すると同時に、高い保磁力が得られることが記載され、例えば熱CVD法によってZnコーティングされた合金粉末の保磁力は12kOeとされている。

【0005】

【発明が解決しようとする課題】 上記したように、Znなどの金属コーティングを施したSm-Fe-N系合金粉末は、耐熱性及び耐食性が改善され且つ高い保磁力が得られるものの、飽和磁化は約10kG以下であり、コーティング前のSm-Fe-N系合金粉末よりも大幅に低下してしまう。これは、金属コーティングによって、保磁力を下げる突起などが平滑化されるため保磁力は高くなるが、粉末同士がコーティングされた金属により相互に接合されて凝集したため、粉末の配向ができずに飽和磁化が低下したものと考えられる。

【0006】 このため、Sm-Fe-N系合金粉末にZnなどの金属をコーティングする際に、粉末の凝集を起こすことなく、高い保磁力を得ると共に、飽和磁化の低下を出来るだけ抑制して、磁気特性の優れた磁石粉末を得るための研究が盛んに行なわれているが、未だに実用的な方法は確立されていない。

【0007】 本発明は、このような従来の事情に鑑み、Sm-Fe-N系合金粉末の耐熱性及び耐食性を改善すると同時に、保磁力及び飽和磁化ともに優れた磁石用Sm-Fe-N系被覆合金粉末、及びその製造方法を提供することを目的とする。

【0008】

【課題を解決するための手段】 上記目的を達成するため、本発明は、Sm-Fe-N系合金粉末の表面の少なくとも一部が融点150～500℃の金属で被覆され、飽和磁化が11kG以上であることを特徴とする磁石用Sm-Fe-N系被覆合金粉末を提供する。

【0009】 また、上記磁石用Sm-Fe-N系被覆合

金粉末の製造方法は、Sm-Fe-N系合金粉末と融点150～500℃の金属粉末を混合し、不活性ガス中200～500℃で熱処理して合金粉末の表面の少なくとも一部を金属で被覆した後、得られた被覆凝集粉末の凝集を解くことを特徴とする。

【0010】この磁石用Sm-Fe-N系被覆合金粉末の製造方法において、被覆凝集粉末の凝集を解く方法としては、被覆凝集粉末を湿式又は乾式にて粉碎する方法、あるいは被覆凝集粉末の表面を被覆している金属の一部を酸又はアルカリの溶液中で溶解する方法がある。

【0011】

【発明の実施の形態】本発明において、Sm-Fe-N系合金粉末と融点150～500℃の金属粉末を不活性ガス中で熱処理することにより、合金粉末の表面を上記低融点の金属で簡単に被覆することができる。上記低融点の金属で被覆された被覆凝集粉末は、粉末同士が互いに接合し凝集した状態となるので、粉末配向時に塊のままで一つずつの粒子にならず、従って磁気特性が低下してしまう。そこで、上記金属の被覆により互いに凝集した被覆凝集粉末の凝集状態を、実質的に個々の粒子が配合できる状態にまで解くことによって、優れた磁気特性が得られる。

【0012】即ち、Sm-Fe-N系合金粉末の粒子は、金属被覆の成形によって突起などの表面欠陥が平滑化されるうえ、逆磁区発生の核が被覆金属と拡散反応することにより減少するため、高い保磁力が得られるものと考えられる。一方、金属被覆によって各粒子が凝集するため磁気特性が落ちるが、粉碎などの方法で粉末の凝集を解くことにより高い磁気特性が得られ、特に飽和磁化の低下を有効に抑制することができる。

【0013】Sm-Fe-N系合金粉末を被覆する金属としては、熱処理により粒子表面の被覆が可能であり、且つ突起などの表面欠陥を平滑に修復できるものであって、被覆金属と合金粉末との間に拡散層が形成されること、更には被覆金属による凝集を解きやすい材料が好ましい。このような被覆金属としては、融点が150～500℃の低融点金属、例えば亜鉛(Zn)、錫(Sn)、インジウム(In)、鉛(Pb)などが挙げられる。特にZnは、420℃以上の温度でFe及びSmと合金を作りやすいので好ましい。

【0014】Sm-Fe-N系被覆合金粉末中における融点150～500℃の被覆金属の含有量は、0.1～9.1重量%の範囲が好ましい。この被覆合金の含有量が0.1重量%未満ではSm-Fe-N系合金粉末を被覆するのに不足し、 iH_c (保磁力)が上らず、逆に9.1重量%を超えると飽和磁化が11kG未満になる。また、Sm-Fe-N系合金粉末の表面を被覆している融点150～500℃の金属の厚みは、一般的に平均で10～5000Åの範囲である。例えば、粒径5μmのSm-Fe-N系合金粉末に5重量%のZn粉末を

添加した場合、Zn被覆の厚みは約440Åとなる。

【0015】Sm-Fe-N系合金粉末を金属で被覆する方法は、Sm-Fe-N系合金の粗粉末又は微粉末を上記Znなどの低融点の金属粉末と混合し、N₂ガスやArガスなどの不活性ガス中において200～500℃で熱処理する。熱処理温度が200℃未満では金属粉末とSm-Fe-N系合金粉末の反応が進まず、逆に500℃を超えるとSm-Fe-N系合金粉末が分解する。尚、Sm-Fe-N系合金粉末への金属粉末の添加量は、上述したように被覆金属の含有量が被覆合金粉末の0.1～9.1重量%となるように、一般的にはSm-Fe-N系合金粉末に対して0.1～10重量%の金属粉末を添加することが好ましい。

【0016】この熱処理によりSm-Fe-N系合金粉末の表面の少なくとも一部に金属が被覆されるが、この被覆金属によって合金粉末同士が凝集しているので、その凝集した被覆凝集粉末を解く必要がある。被覆凝集粉末の凝集を解く方法には特に制限はなく、凝集の程度や被覆金属の材質に応じて適宜選択すればよい。

【0017】凝集を解くための好ましい方法の一つとして、凝集した被覆凝集粉末を湿式又は乾式にて解砕する方法がある。例えば、アトライターにより溶媒中で150～300rpm、5分～3時間粉碎することにより、被覆合金粉末の凝集を解くことができる。また、被覆凝集粉末の凝集と解く別の方法としては、酸又はアルカリの溶液を用いて被覆金属を溶かし出すことにより、被覆凝集粉末の凝集を解くことができる。

【0018】尚、Sm-Fe-N系合金粉末については、特に制限はないが、磁石用として一般的に使用されている合金組成、具体的には、Smを必須元素とする少なくとも1種の希土類元素5～15原子%と、窒素0.5～2.5原子%と、残部の鉄又は一部をコバルトで置換した鉄とからなる合金組成であってよい。また、かかるSm-Fe-N系合金粉末の製造法も特に限定されず、例えば、Sm-Fe合金粉末を溶解合金法若しくは特公平3-62764号公報に記載されているような還元拡散法により製造し、その後このSm-Fe合金粉末を窒化して製造することができる。更に、特開平5-148517号公報に記載されているような還元拡散法の応用、即ち還元拡散反応で得られた焼結体を窒化後に湿式処理して製造することもできる。これらの方法の中では、製造コストの点で還元拡散法の適用が特に優れている。

【0019】このようにして得られる本発明のSm-Fe-N系被覆合金粉末は、Znなどの金属被覆の形成によって優れた耐熱性及び耐食性を備えると同時に、高い保磁力が得られ、しかも粉末の凝集が解かれて実質的に個々の粒子が配向できる状態に独立しているため、11kGを超える高い飽和磁化を有している。

【0020】

【実施例】実施例1

還元拡散法により25重量%のSmを含むSm-Fe合金粉末を製造した。即ち、純度99.9重量%、粒度150メッシュ（タイラー標準、以下同じ）以下の電解Fe粉と、純度99重量%、平均粒度325メッシュの酸化Sm粉末と、純度99重量%の粒状金属Caとを、Vブレンダーを用いて混合した。得られた混合物をステンレス容器に入れ、Ar雰囲気中にて1150℃で8時間加熱して還元拡散反応させた。次いで、この反応生成物を冷却し、水中に投入して崩壊させた。得られたスラリーを水洗し、更に酢酸を用いて酸洗浄して未反応Caと副生したCaOを除去した後、濾過してエタノールで置換し、真空乾燥して粒径150μm以下の25重量%Sm-Fe合金粉末を得た。

【0021】このSm-Fe合金粉末を100μm以下に篩い分けし、水素-アンモニア混合ガス中において480℃で270分保持することにより窒化した後、冷却

して取り出した。得られたSm-Fe-N合金粉末の組成は、Smが24.1重量%、Feが72.4重量%、Nが3.5重量%であった。

【0022】このSm-Fe-N合金粉末1kgに対して下記表1に示す添加量のZn粉末を混合し、更にアトライターで200rpm、60分混合を兼ねて粉碎した。その後、Arガスを1リットル/minで流しながら、430℃で10時間熱処理し、室温まで冷却した後取り出した。得られた被覆凝集粉末は表面がZnで被覆され且つ凝集しているので、更にアトライターで溶媒中にて200rpm、20分粉碎した後、乾燥してSm-Fe-N系被覆合金粉末を得た。熱処理直後の被覆凝集粉末と、粉碎後のSm-Fe-N系被覆合金粉末について、それぞれVSMにより磁気特性を測定し、その結果を下記表1に示した。

【0023】

【表1】

試料	Zn添加量 (wt%)	熱処理直後の被覆凝集粉末		粉碎後の被覆凝集粉末	
		飽和磁化(kG)	保磁力(kOe)	飽和磁化(kG)	保磁力(kOe)
1*	0	14.3	7.2	12.9	8.8
2*	0.05	14.3	7.2	13.0	8.7
3	1	10.6	9.3	12.8	10.5
4	2	10.2	9.6	12.5	11.0
5	3	9.2	10.4	11.8	11.7
6	4	8.9	11.0	11.5	12.4
7	7	8.4	12.4	11.3	14.5
8	10	7.9	15.1	11.1	17.8
9*	12	7.5	17.1	10.7	18.9

(注) 表中の*を付した試料は比較例である。

【0024】上記表1の結果から分かるように、Znを添加しない試料1及びZn添加量の少ない試料2と比較して、本発明の試料3～8は、熱処理直後の被覆凝集粉末では保磁力は2～8kOe程度高くなっているものの、凝集のため飽和磁化は最大6.4kG低くなっている。しかし、粉碎後の凝集が解かれた試料3～8の被覆合金粉末では、11.1～12.8kGと高い飽和磁化が得られた。また、Znの添加量が多い試料9は飽和磁化が11kG未満である。

【0025】実施例2

上記実施例1と同様にしてSm-Fe-N系合金粉末にZnを被覆した被覆凝集粉末を作製し、この被覆凝集粉末10gを純水で100倍に薄めた酢酸水溶液200ml中に投入して3分攪拌した後、乾燥して凝集の解かれ

たSm-Fe-N系被覆合金粉末を得た。上記被覆凝集粉末の飽和磁化は10.2kGであったが、凝集が解かれた被覆合金粉末の飽和磁化は12.8kGまで高められた。

【0026】実施例3

上記実施例1で最終的に得られた各試料のSm-Fe-N系被覆合金粉末の耐熱性を確認するため、各試料10gをオープンに入れ、真空中にて230℃で1時間保持した。その後、耐熱性試験後の被覆合金粉末について実施例1と同様に磁気特性を測定し、その結果を下記表2に示した。

【0027】

【表2】

試料	Zn添加量 (wt%)	粉碎後の被覆凝集粉末		耐熱試験後の被覆合金粉末	
		飽和磁化(kG)	保磁力(kOe)	飽和磁化(kG)	保磁力(kOe)
1*	0	12.9	8.8	12.4	6.1
2*	0.05	13.0	8.7	12.4	6.2
3	1	12.8	10.5	12.5	9.2
4	2	12.5	11.0	12.2	9.8
5	3	11.8	11.7	11.5	10.3

6	4	11.5	12.4	11.3	11.0
7	7	11.3	14.5	11.2	13.4
8	10	11.1	17.8	11.1	16.7
9*	12	10.7	18.9	10.7	18.7

(注) 表中の*を付した試料は比較例である。

【0028】上記表2の結果より、本発明の試料3～8は、Zn被覆により耐熱性が向上していることが分かる。即ち、Zn被覆を施していない試料1及びZn添加量の少ない試料2では、耐熱試験後の保磁力が6.1～6.2kOeまで低下しているのに対して、Zn被覆を行った本発明の試料3～8では9kOe以上の保磁力が保たれている。

試料のSm-Fe-N系被覆合金粉末の耐食性を確認するため、各試料10gを70℃、湿度80%の恒温恒湿槽に入れ、10時間保持した。その後、耐食性試験後の被覆合金粉末について実施例1と同様に磁気特性を測定し、その結果を下記表3に示した。

【0030】

【表3】

【0029】更に、上記実施例1で最終的に得られた各

試料	Zn添加量 (wt%)	粉砕後の被覆凝集粉末		耐食試験後の被覆合金粉末	
		飽和磁化(kG)	保磁力(kOe)	飽和磁化(kG)	保磁力(kOe)
1*	0	12.9	8.8	12.1	5.8
2*	0.05	13.0	8.7	12.1	5.9
3	1	12.8	10.5	12.2	8.2
4	2	12.5	11.0	12.0	9.0
5	3	11.8	11.7	11.4	9.5
6	4	11.5	12.4	11.1	10.2
7	7	11.3	14.5	11.1	12.1
8	10	11.1	17.8	11.0	14.9
9*	12	10.7	18.9	10.5	16.9

(注) 表中の*を付した試料は比較例である。

【0031】上記表3の結果より、本発明の試料3～8はZn被覆により耐食性の向上が明らかである。即ち、Znを被覆していない試料1及びZn添加量の少ない試料2では、耐食性試験後の保磁力が5.8～5.9kOeまで低下しているのに対し、Zn被覆を行った本発明の試料3～8では耐食性試験後も8kOe以上の保磁力が保たれている。

前記実施例1と同様にしてSm-Fe-N系被覆合金粉末を製造したが、添加混合する金属粉末はZn粉末、In粉末又はSn粉末を使用し、且つその添加量を3重量%とした。得られた各被覆合金粉末について、実施例1と同様に磁気特性を測定し、その結果を下記表4に示した。

【0033】

【表4】

【0032】実施例4、

試料	添加金属	熱処理直後の被覆凝集粉末		粉砕後の被覆凝集粉末	
		飽和磁化(kG)	保磁力(kOe)	飽和磁化(kG)	保磁力(kOe)
10*	無し	14.3	7.2	12.9	8.8
11	Zn	9.2	10.4	11.8	11.7
12	In	9.8	8.2	12.3	9.9
13	Sn	9.3	7.8	12.0	9.5

(注) 表中の*を付した試料は比較例である。

【0034】上記表4の結果から分かるように、低融点の金属粉末を添加しない試料10と比較して、本発明の試料11～13は、熱処理直後の被覆凝集粉末では保磁力は1～3kOe程度高くなっているものの、凝集のため飽和磁化は最大5kG低くなっている。しかし、粉砕後の凝集が解かれた試料11～13の被覆合金粉末では、11.8～12.3kGの高い飽和磁化が得られた。

被覆合金粉末の耐熱性を確認するため、前記実施例3と同様に、各試料10gをオープンに入れ、真空中にて230℃で1時間保持した。その後、耐熱性試験後の被覆合金粉末について、上記実施例1と同様に磁気特性を測定し、その結果を下記表5に示した。

【0036】

【表5】

【0035】上記で得られた各試料のSm-Fe-N系

試料	添加金属	粉砕後の被覆凝集粉末		耐熱試験後の被覆合金粉末	
		飽和磁化(kG)	保磁力(kOe)	飽和磁化(kG)	保磁力(kOe)

10*	無し	12.9	8.8	12.4	6.1
11	Zn	11.8	11.7	11.5	10.3
12	In	12.3	9.9	12.1	8.8
13	Sn	12.0	9.5	11.9	8.5

(注) 表中の*を付した試料は比較例である。

【0037】上記表5の結果より、本発明の各試料はZn、In、Snの被覆により耐熱性が向上したことが明らかである。即ち、被覆を施していない試料10に比較し、Zn、In、Snを被覆した本発明の試料11～13では、耐熱試験後の保磁力が2.4～4kOe程度高くなっている。

【0038】更に、上記で得られた各試料のSm-Fe

-N系被覆合金粉末の耐食性を確認するため、前記実施例3と同様に、各試料10gを70℃、湿度80%の恒温恒湿槽に入れ、10時間保持した。その後、耐食性試験後の被覆合金粉末について実施例1と同様に磁気特性を測定し、その結果を下記表6に示した。

【0039】

【表6】

試料	添加金属	粉砕後の被覆凝集粉末		耐食試験後の被覆合金粉末	
		飽和磁化(kG)	保磁力(kOe)	飽和磁化(kG)	保磁力(kOe)
10*	無し	12.9	8.8	12.1	5.8
11	Zn	11.8	11.7	11.4	9.5
12	In	12.3	9.9	12.1	9.1
13	Sn	12.0	9.5	11.9	8.8

(注) 表中の*を付した試料は比較例である。

【0040】上記表6の結果より、本発明の各試料はZn、In、Snの被覆により耐食性の向上が明らかである。即ち、被覆を施していない試料10に比較し、Zn、In、Snを被覆した本発明の試料11～13では、耐食試験後の保磁力が3～3.5kOe程度高くなっている。

【0041】

【発明の効果】本発明によれば、ニュークリエーションタイプの保磁力発生機構を有するSm-Fe-N系合金粉末の表面に、簡単にZnなどの金属被覆を形成でき、

更に金属被覆された被覆凝集粉末の凝集を粉砕などにより解くことによって、耐熱性及び耐食性に優れると同時に、8kOe以上の高い保磁力が得られ、且つ11kGを超える高い飽和磁化を有するSm-Fe-N系被覆合金粉末を安価に提供することができる。従って、この被覆合金粉末は、ニュークリエーションタイプの保磁力発生機構を有する磁気特性に優れたSm-Fe-N系の磁石粉末であり、各種FA用アクチュエーターや回転機用の磁石用として有望である。

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